

Synthetic Organic Chemicals

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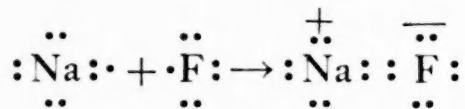
OCTOBER, 1934

No. 1

Types of Valence

THE electronic theory of valency, which explains the various types of valence and chemical union on the basis of the distribution of the electrons of the atoms concerned, represents one of the most important advances in recent chemistry. By this means, many of the phenomena formerly considered anomalous or unusual are shown to have a rational basis.

There are possible at least two types of chemical combination. The first involves a passage of at least one electron from one element to another as in the case of sodium fluoride:



Sodium, with an extra electron (beyond the stable shell of eight), readily loses this electron to the fluorine atom which has seven in its outer group, so that both atoms form stable octets. This results in each being charged, and an electrolyte is formed.

Such a union is called electrovalency; it is found in general when an electropositive element or radical unites with an electronegative element or radical. Salts, the typical products of such linkages, are highly polar substances. Inasmuch as the transfer of electrons in the case of salts is nearly or entirely complete, a strong electrical field is

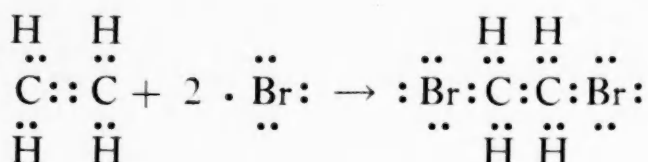
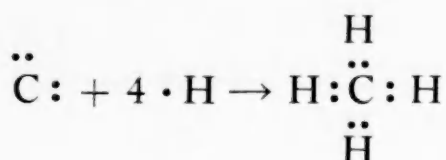
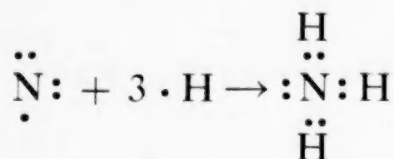
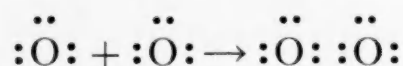
produced which tends to hold the ions together strongly. Thus, the typical salts have high melting points, high boiling points, and high heats of vaporization. They appear to be completely ionized even in crystalline form, so that their crystal lattice is made up of a regular, though sometimes complex, arrangement of ions. In the molten state, the forces holding the ions in the crystal lattice are broken down, and the mobile ions are good conductors of electricity. Another characteristic of electrovalent compounds is their solubility in associated solvents and insolubility in non-associated solvents such as most typical organic liquids.

The second type of chemical combination, called by Langmuir "covalency," resulting when electrons are shared between two elements, is very common in organic compounds. Such sharing of electrons takes place in pairs or duplets except for a few cases, such as SF₆, OsF₈, etc. The explanation in these cases appears to be either links of single shared electrons or the presence of more than eight electrons in the outer shell of one of the atoms.

The pair of electrons shared between two atoms is the equivalent of the ordinary valence bond. Similarly, a double bond is the sharing of four electrons between two atoms.

In the case of a normal covalency

one electron of each shared pair is contributed by each atom, thus:



Such unions do not in general ionize, and so are practically nonconducting either in the molten state or in solution. Not nearly so great an electrical field is produced by this sharing as is caused by an actual transfer of an electron, and there is a relatively smaller force holding the molecules together. Consequently, covalent compounds are more volatile and have lower melting points and heats of vaporization than electrovalent compounds. They are generally soluble in non-associated liquids of low dielectric constant and have low solubility in water, the typical solvent for electrovalent compounds.

According to Fajans's theory, the high electrostatic attraction between the ions of an electrovalent compound brings about a distortion of the field of the outer electrons. If the attraction be great enough, a point will be reached at which the distorted orbits will be less stable than orbits enclosing both nuclei, and so an electrovalency will pass over into a covalency.

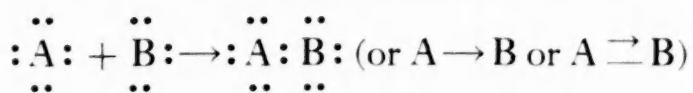
Polyvalence favors this change as there is more electrical attraction. So does small size of the cation, as the smaller it is (for a given charge) the

more strongly it attracts the anion. Large size of the anion also favors the change from an electrovalence to a covalence, as the electrons are less firmly held when farther from the nucleus.

An examination of the conductivity and volatility of the hydrides and the chlorides of the elements confirms this theory strikingly; these compounds of the heavier elements of high valence being volatile and poor conductors—the corresponding compounds of the lighter elements of low valence are non-volatile and good conductors. The two classes are fairly definitely marked, the division being roughly approximated by a diagonal from upper left to lower right as the periodic table is usually written. In some cases, as for example tin, the compounds of different valence fall into different groups.

Hydrogen occupies a unique position in the periodic table on account of the stability of the first electron shell containing two electrons. Thus, hydrogen can form a positive ion as in its halides, by losing an electron; or it can gain an electron and form a negative radical, as the hydrides of the alkalis. Also, it can readily form covalent linkages, as in methane and similar compounds.

A special case of covalency is the union formed between two atoms when both the shared electrons are provided by only one of the atoms concerned:



This type is called co-ordinate valence.

Although the bond shown above is represented by a double bond according to the classical representation, it consists of a sharing of a pair of electrons, and shows many of the characteristics of a single bond.

This concept is of such importance in explaining many phenomena that it will be discussed separately later.

Oxidation of Fatty Acids

THE mechanism of oxidative reactions of fatty acids differs greatly with the structure of the substrate and the nature of the oxidizing agent. The insolubility of the higher fatty acids in non-oxidizable media, their tendency to form soapy emulsions, and the difficulties of separating the mixtures of homologues limit the experimental treatment of the problem.

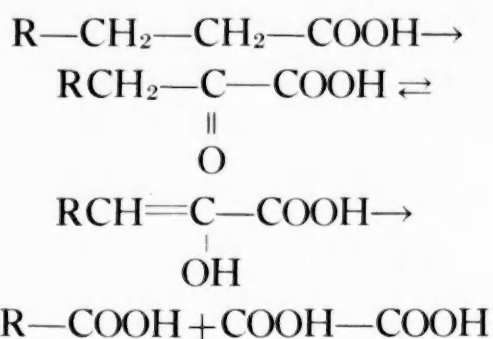
With the normal saturated acids, most substitutions, condensations, and other reactions occur at the carbon adjacent to the carboxyl group: the α -carbon. Acid oxidants such as chlorine or chromic acid act on this carbon almost exclusively. Nitric acid forms an exception, attacking the very resistant terminal methyl group with the formation of dicarboxylic acids.

In the animal body the fatty acids are oxidized two carbons at a time (Knoop, 1904). Dakin's discovery concerning the reactivity of the β -carbon has been widely accepted as an explanation of this phenomenon. Under conditions similar to the ones encountered in the living organism (hydrogen peroxide in neutral medium), fatty acid soaps yield small traces of β -keto acids and copious amounts of the corresponding methyl ketones (Dakin, 1908). This mechanism explained satisfactorily the occurrence of β -keto butyric acid among the end products of incomplete fat metabolism (e.g. in diabetes).

Recently it was found that the oxidation with hydrogen peroxide is not limited to the α - and β -carbons. By the isolation of γ - and δ -ketones and succinic acid, and comparing the products with synthetic ones, it could be shown that the γ - and δ -carbons are also polar to a considerable degree (Clutterbuck and Raper, 1925).

That the point of rupture is not nec-

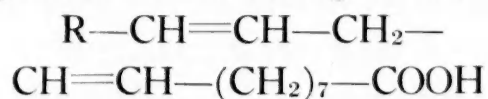
essarily identical with the point of primary attack has been borne out by the investigations of W. L. Evans (1916 and later) and his student E. J. Witzemann (1932). In alkaline medium, enolization may lead to a shift in the point of rupture:



This type of conditioned mechanism is finding wide application in the explanation of oxidative phenomena.

Ethylenic linkages, branched chains, and other reactive groups such as hydroxyl, render the fatty acid molecule rather vulnerable to oxidation. These modified reactions, however, are more characteristic of the particular type of bond or group than of the fatty acids themselves. Highly unsaturated acids exhibit autoxidative polymerization as do other non-acidic unsaturated compounds. On the other hand, amyl alcohol and the corresponding isovaleric acid yield, under the same experimental conditions, identical products of oxidation, namely, acetone, acetic and malonic acids.

The prevalence of the 9-10 position of the first ethylenic linkage and the avoidance of conjugated systems in naturally occurring unsaturated acids are very characteristic features as yet entirely unexplained. These acids usually possess the following structure:



The behavior of this type of linkage in autoxidations is not very well known.

Eastman Organic Chemicals as Analytical Reagents

XXXIV REAGENTS FOR TIN

CUPFERRON

A. Kling and A. Lassieur, *COMPT. REND.* 170, 1112 (1920), also N. A. Furman, *IND. AND ENG. CHEM.* 15, 1071 (1923)

Tin can be quantitatively precipitated from a fluoborate solution by cupferron. Copper, lead, trivalent arsenic and antimony can be separated from stannic tin by precipitation from a hydrofluoric acid solution with hydrogen sulfide. Boric acid is added to the filtrate after which it is boiled to expel hydrogen sulfide. An excess of a 10% solution of cupferron is added, which forms a white precipitate of the stannic salt. Any separated sulfide is dissolved by the addition of hydrogen peroxide and the excess of the latter removed by boiling. The precipitate is stirred until compact and brittle, washed with cold water, carefully ignited to the oxide and weighed.

DIMETHYLGLYOXIME

F. Feigl, *CHEM. ZTG.* 43, 861 (1919)

Stannous salts can be determined indirectly by their reducing action on ferric salts through the formation of a complex ferrodimethylglyoxime. One drop of the solution under test, which should be strongly acid and which contains tin in the bivalent form, is mixed with one drop of a 0.1N ferric chloride solution and after one minute a small crystal of tartaric acid added. After

solution of the acid one drop of a 1% alcoholic solution of dimethylglyoxime is added and then ammonia. If tin is present, a more or less intense red coloration due to ferrodimethylglyoxime is formed. Sensitivity 1:1,250,000.

PHENYLARSONIC ACID

Knapper, Craig, and Chandlee, *J.A.C.S.* 55, 3945-7 (1933)

Tin is precipitated quantitatively by adding to a hot acid solution of the metal a saturated solution of phenylarsonic acid. The sample, 0.1 gram, is dissolved in 10 cc. of 1:1 nitric acid and heated gently to complete the oxidation and until excess nitric acid is removed. Hydrochloric acid is added dropwise to completion of solution and diluted to 150-200 cc. with water. The acidity is adjusted to 5% HCl by volume. The solution is heated and 35 cc. of a saturated aqueous solution of phenylarsonic acid added. After standing, the mixture is filtered, the precipitate washed with 4% ammonium nitrate until free from chlorides, ignited gently and weighed as stannic oxide. Zirconium and thorium are the only elements commonly associated with tin which interfere. If iron is present, the washed precipitate is redissolved in 5 cc. hot concentrated hydrochloride diluted to 150 or 200 cc. and reprecipitated with 15 cc. of the reagent. The procedure is then continued as before.

New Eastman Organic Chemicals

T 3718	1-Aminobenzene-2,5-disulfonic Acid (40% Paste)	
	(Technical)	1 kg. \$ 7.50 E
3693	γ -Chlorobutyronitrile BP 93-96°/26 mm.....	100 g. ... 15.00 C
3704	2,4-Dichloro-1-naphthol MP 107-108°.....	100 g. ... 4.00 C
2416	β -Methylnaphthalene MP 34-35°.....	1 kg... 6.50 E